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Pesticide Fact Sheet Number 236: Pyridate

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This document contains up-to-date chemical information, including a summary of the Agency's regulatory position and rationale, on a specific pesticide or group of pesticides. A Fact Sheet is issued after one of the following actions has occurred.

1. Issuance or reinssuance of a registration standard,
2. Issuance of each special review document,
3. Registration of a significantly changed use pattern,
4. Registration of a new chemical, or
5. An immediate need for information to resolve controversial issues relating to a specific chemical or use pattern.

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Pesticides, regulations, Chemical Information Fact Sheet, Use Patterns, science findings.

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EPA

Pesticide Fact Sheet

PB93-130441

Name of Chemical: PYRIDATE
Reason for Issuance: PESTICIDE REGISTRATION
Date Issued: OCTOBER 23, 1992
Fact Sheet Number: 236

DESCRIPTION OF CHEMICAL

Generic Name:	[o-(6-chloro-3-phenyl-4-pyridazinyl)-S-octyl-carbonothioate]
Other Names:	6-chloro-3-phenylpyridazin-4-yl-S-octyl-thiocarbonate (IUPAC), S-octyl thiocarbonate (C.A. 9th collective index), CL 11.344
Common Name:	Pyridate
Trade Name:	Tough
EPA Shaughnessy Codes:	128834-9 & 128835
Chemical Abstracts Service (CAS) Number:	55512-33-9
Year of Initial Registration:	1992
Pesticide Type:	Herbicide
U.S. and Foreign Producers:	Agrolinz, Incorporated

USE PATTERNS AND FORMULATIONS

Application Sites:
Tough 45 WP - Use on cabbage and field corn
Tough 3.75 EC - Use on peanuts and field corn
Pyridate Technical

Types and Methods of Application:
Ground application (boom sprayer)

Application Rates:
Tough 45 WP (wettable powder)
The maximum application rate is 2 pounds of product [0.9 lbs. active ingredient (ai)/acre (A)] on cabbage. One application per use season.

Tough 3.75 EC (emulsifiable concentrate)
The maximum application rate is 3 pints of product (1.44 lbs. ai)/A on peanuts. One application per use season.

The maximum application rate is 2 pints of product (0.96 lbs. ai)/A on corn.

Types of Formulations:
Tough 45 WP - A wettable powder containing 0.45 lbs. ai/ per lb. of product.

Tough 3.75 EC - An emulsifiable concentrate containing 3.75 lbs. ai/ per gallon of product.

Major Uses:
Tough 45 WP is used for postemergent selective control of broadleaf weeds in cabbage.

Tough 3.75 EC is used for postemergent selective control of broadleaf weeds in peanuts and corn.

SCIENCE FINDINGS

Summary Science Statement

Ample toxicological, ecological effects and dietary exposure data have been submitted to support the conditional registrations of Pyridate. The terms of the conditional registration will require the registrant to submit an updated anaerobic metabolism study.

The Environmental Fate and Ground Water Branch (EFGWB) has sufficient data to assess the environmental fate of Pyridate. The following data requirements have been satisfied: hydrolysis, aerobic soil metabolism and accumulation in fish. The data requirements for leaching and adsorption/desorption are fulfilled. Data requirements concerning the mobility of unaged pyridate in four soils and aged pyridate residues in one soil have been satisfied. Laboratory and field volatility requirements were waived on the basis that pyridate and its main degradate, CL-9673 have very low vapor pressure. The

field dissipation studies are adequate to support the conclusion that the use of this chemical on the proposed crops has very little if any potential to result in residues of the degradate leaching into ground water.

Chemical Characteristics of the Technical Material and the Formulations

Purified Active Ingredient (PAI)
91% Technical Grade of the Active Ingredient (TGAI)
Celsius (C)
Not Required (N.R.)
Not Applicable (N.A.)

	45WP	Tough 3.75 EC	Tech
Color:	dark brown with slight turbidity to slightly yellowish white (PAI)	clear brown	dark brown w/slight turbidity or sediment
Physical State:	powder, liquid at 25 C, partially crystallized at <20 C (TGAI) crystalline (PAI)	liquid at 25 C	oily liquid @ 25 C; crystallizes slowly <20 C
Odor:	similar to a mixture of camphor and mercaptane-sulfur compounds	putrid mercaptane-like smell (TGAI)	typical of mercaptane & sulfur cmpnds
Molecular Weight:	378.9		
Empirical Formula:	$C_{19}H_{23}ClN_2O_2S$		
Boiling Point:	above 220 C at 0.14 mbar (TGAI)	N.R.	decomposes before boiling
Melting Point:	liquid at 20-25 C (TGAI) and 27 C (PAI)	N.R.	liquid @ room temp

	45WP	Tough 3.75EC	Tech
Vapor Pressure:	1.33 X 10^{-9} mbar at 20 C 7.49 x 10^{-9} torr. at 25 C (PAI)	N.R.	7.49x10^{-9} torr. @ 25 C
Dissociation Constant:	Technical pyridate has a low solubility in water and is not ionic; therefore, dissociation in water is negligible (TGAI)		
Density, bulk density, or specific gravity:			1.167 at 20 C/ 20 C

		---	0.245
Solubility in various solvents:	1.49 ± 0.24 ppm in water (PAI)		
			>900 g/100 mL of kerosene, xylene, ethyl acetate, acetone, cyclohexane, & N-methyl-pyrrolidone (TGAI)
Octanol/water partition coefficient:	PAI P = 11,100 ± 4000 (log P = 4.01 ± 0.16) P = 71.22 at pH 5, 23.4 at pH 6, and 3.19 at pH 7 (CL-9673)	N.R.	N.R.
pH:	N.R.		non-dissoc. organic liquid

Stability:

(TGAI) Loss of AI: 8.7 and 30.2% from pyridate stored

at 50 C for 730 days and 75 C for 168 days, respectively. Analysis was by HPLC (TGAI). A sample of pyridate stored in a glass bottle in sunlight for 1 year did not show accelerated decomposition. Storage of pyridate in mild steel drums did not lead to accelerated decomposition. In the presence of moisture, slow corrosion of steel and zinc occur. No catalytic effects of metal ions on decomposition was noted (TGAI).

(3.75 EC) N.R.

(45 WP) N.R.

Oxidizing or reducing action:

(TGAI) The structural formula of pyridate does not contain functional groups which are known for their oxidizing properties such as aromatic or aliphatic $-NO_2$ or peroxy-groups. Also strong reducing functional groups such as $R-NH-NH_2$ or R-NH-OH are not present. These facts agree with ther egistrant's findings about the reactivity of the TGAI, which suggest that this product does not possess any strong oxidizing or reducing potential.

(3.75 EC) Neither stated by the registrant

(45 WP) Neither stated by the registrant

Flammability:

flash point=97 F flash point= 131 C (TGAI)

Explodability:

(TGAI) The structural formula of pyridate does not contain functional groups known to result in explosive properties, such as aromatic or aliphatic, peroxy-, azo, azido or $R-O-NO_2$. These facts agree with registrants findings about the reactivity of the TGAI, which suggest that the TGAI poses no explosive hazard (TGAI).

(3.75 EC) has no explosive potential

(45 WP) has no explosive potential

Storage stability:

(TGAI) Following 2-years storage in glass bottles at 20-27 C, samples of pyridate did not show significant degradation as determined by HPLC analysis and comparison of initial samples stored at -28 C (TGAI).

Storage Stability

(3.75 EC) Neither degradation of the AI nor a deterioration of emulsion stability was noticed after 22 months when stored at ambient temperatures in aluminum bottles.

(45 WP) Degradation of the AI is negligible and deterioration of suspensibility was not significant after 36 months when stored at ambient temperatures in tightly sealed bags from aluminized polyester-foil with an inner lining of polyethylene.

	45WP	Tough 3.75EC	Tech
Viscosity:		8.1 mm^2/s	369 mPas @ 20 C & 79 mPas @ 40 C (TGAI)
Miscibility:	N.R.	N.A.	N.A.

Corrosiveness:

(TGAI) Not corrosive to aluminum 99.5%; mild steel, type H II at 40 C as illustrated by a corrosion rate of <0.01 g/m^2h (negligible) from mass loss. In addition, the CrNiMo-steel (18/10/2) thin film evaporator used in the production of the TGAI has shown no significant corrosion following 2 yrs of contact with TGAI at 140 C.

(3.75 EC) It is not corrosive to aluminum. It does not chemically attack HD-polyethylene nor poly-amide-modified polyethylene. A certain permeability of normal HD-polyethylene for the solvent was detected.

(45 WP) It is not corrosive to aluminized polyester-foil with PE inner lining.

Toxicology Characteristics

Male (M)

Female (F)

Acute Toxicity (Technical)

Acute Oral Toxicity:
Toxicity Category: III
Rat: LD_{50} 5993 mg/kg (M)
LD_{50} 3544 mg/kg (F)

Acute Dermal Toxicity:
Toxicity Category: III
Rabbit: LD_{50} > 2000 mg/kg(M/F)

Acute Inhalation Toxicity:
Toxicity Category: III
Rat: LC_{50} > 4370 mg/m^3 (M/F)

Primary Dermal Irritation:
Toxicity Category: III
Moderate irritant

Primary Eye Irritation:
Toxicity Category: IV
Non irritant

Dermal Sensitization:
Sensi-tizer

Acute Toxicity (3.75 EC and 45 WP formulations)

Acute Oral Toxicity (3.75 EC):
Toxicity Category: III
Rat: LD_{50} 1871 mg/kg (M)
LD_{50} 905 mg/kg (F)
LD_{50} 1258 mg/kg (M/F)

Acute Oral Toxicity (45 WP):
Toxicity Category: III
Rat: LD_{50} 2205 mg/kg (M)
LD_{50} 2377 mg/kg (F)
LD_{50} 2330 mg/kg (M/F)

Acute Dermal Toxicity: (3.75 & 45 WP)
Toxicity Category: III
Rabbit: LD_{50} > 2000 mg/kg (M/F)

Acute Inhalation Toxicity (3.75 EC):
Toxicity Category: III
Rat: LC_{50} 3832 mg/m^3 (M)
LC_{50} 2904 mg/m^3 (F)
LC_{50} 3282 mg/m^3 (M/F)

Acute Inhalation Toxicity (45 WP):
Toxicity Category: III
Rat: LC_{50} 2140 mg/m^3 (M/F)

Primary Eye Irritation (3.75 EC):
Toxicity Category: III
Moderate eye irritant

Primary Eye Irritation (45 WP):
Toxicity Category: III
Positive eye irritant, irritation reversed by day 7

Primary Dermal Irritation (3.75 EC):
Toxicity Category: III
Slight irritant

Primary Dermal Irritation (45 WP):
Toxicity Category: III
Non-irritating

Dermal Sensitization: (3.75 EC & 45 WP)
Sensitizer

Subchronic toxicity:

A 90-day feeding study in rats administered Pyridate technical (via oral gavage) at dosage levels of 0, 62.5, 177, 500 and 500/600 mg/kg/day resulted in high toxicity and mortality at the dose level of 500 mg/kg/day (the highest dose tested - HDT). The systemic No-Observable-Effect-Level (NOEL) was 62.5 mg/kg/day and the Lowest-Effect-Level (LEL) was 177 mg/kg/day based on hypoactivity and salivation in both sexes.

A 90-day feeding study in beagle dogs treated with gelatin capsules at dose levels of 0, 20, 60, 200 mg/kg/day caused severe toxicity and mortality at the dose level of 200 mg/kg/day. The systemic NOEL was 20 mg/kg/day (the lowest dose tested - LDT) in both sexes and the LEL was 60 mg/kg/day based on signs of emesis and ataxia.

In a subchronic 21-day dermal study, groups of five male and female rats were dosed by the dermal route with Pyridate at dose levels of 0, and 1000 mg/kg/day. No systemic toxicity was observed. The NOEL was greater than 1000 mg/kg/day.

Chronic Feeding:

Rodent Feeding Studies:

A 2-year chronic feeding rat study treated with 0, 80, 400 and 2500 ppm (analytical levels of 0, 43, 216 and 1350 ppm; 0, 2.2, 10.8 and 67.5 mg/kg/day) of Pyridate technical noted a systemic NOEL of 10.8 mg/kg/day and a LEL of 67.5

mg/kg/day based upon body weight depression. No carcinogenic potential was observed at any dose level.

A new 18 month carcinogenicity study was submitted in 1992. Mice were fed pyridate for 18 months at 0, 400, 800, 1600, and 7000 ppm; doses were equivalent, respectively, to 47.7, 97.1, 169.5, and 882.6 mg/kg/day in males, and 54.5, 114.6, 204.3, and 1044.6 mg/kg/day in females. No statistically significant increases in tumor incidence relative to controls were observed in either sex at any dose. This study satisfied the guideline requirements for a carcinogenicity study in mice.

Non-rodent feeding studies:

In a 1-year feeding study, dogs were treated with Pyridate at doses of 0, 5, 20, and 60 mg/kg/day for the first 34 weeks. After week 34 the dose levels were escalated to 30, 100, and 150 mg/kg/day because there were no toxic signs or effects. The systemic NOEL was 20 mg/kg/day and the LEL was 100 mg/kg/day based on excessive salivation, ataxia (loss of muscle coordination), mydriasis (prolonged or abnormal dilatation of the pupils), dyspnea (difficulty in breathing), tremors, increased respiration and prostration.

Developmental Toxicology:

A rat developmental toxicity study using doses of 0, 55, 165, 400 and 495 mg/kg/day had a developmental NOEL of 165 mg/kg/day and the LEL was 400 mg/kg/day based on increased incidence of missing and/or unossified sternebrae and decreased fetal body weight. The maternal NOEL was 165 mg/kg/day and the LEL was 400 mg/kg/day based on mortality and decreased body weight. The developmental NOEL was greater than 495 mg/kg/day (HDT). The developmental toxicant NOEL was 165 mg/kg/day and the LEL was 400 mg/kg/day based on decreased fetal body weight, increased incidence of missing and/or unossified sternebrae. The Toxicology Branch concluded that Pyridate Technical was not teratogenic when administered to rats from day 6 through 15 of pregnancy.

A rabbit developmental toxicity study using doses of 0, 150, 300 and 600 mg/kg/day of Pyridate had a maternal NOEL of 300 mg/kg/day and a LEL of 600 mg/kg/day based on body weight depression. The developmental NOEL was greater than 600 mg/kg/day (HDT).

Reproduction:

A multigeneration reproduction study in the rat treated with 0, 80, 400 and 2500 ppm (analytical levels of 0, 43,

216, and 1350 ppm) of Pyridate had a maternal NOEL of 10.8 mg/kg/day and a LEL of 67.5 mg/kg/day based on body weight depression. The developmental NOEL was 10.8 mg/kg/day and the LEL was 67.5 mg/kg/day based on body weight loss.

Mutagenicity:

No mutagenic activity was observed when tested in Salmonella typhimurium. Pyridate assayed with and without activation induced cytotoxic effects in chinese hamster ovary (CHO) cells, but it was not clastogenic. Pyridate did not induce somatic mutation in mouse embryos. Pyridate was negative in the in vivo - in vitro unscheduled DNA synthesis in the Sprague Dawley rat.

Physiological and Biochemical Characteristics

Mechanism of Pesticidal Action:
Inhibits the Hill reaction of photosynthesis

Metabolism and Persistence in Plants and Animals:
Based on the available data, the major degradate, CL-9673, appears to have those properties and characteristics associated with known ground-water contaminants. However, the data also indicates that leaching is likely to occur only in extraordinary circumstances, and then with virtually no toxicological effect.

Environmental Characteristics

Hydrolysis
hydrolyzes at pHs 5, 7, and 9

Aerobic Soil Metabolism
CL-9673 degrades with half-lives ranging from 10-27 days.

Mobility (acceptable)
Available data indicates pyridate degrades rapidly and no groundwater contamination should occur.

Dissipation (acceptable)
Available studies indicate that accurate halflife of CL-9673 is difficult to obtain since it is being produced from parent pyridate and at the same time degrading to other compounds.

Accumulation (acceptable)
Residues were not detected in lettuce or carrots above the detection limit of 0.01 ppm equivalent CL-9673. Residues were detected in barley straw

and grain and therefore the accumulation is unacceptable.

(acceptable) Pyridate plus CL-9673 bioaccumulates in bluegill sunfish with a bioconcentration factor of 116.

Review of the data indicates Pyridate degrades rapidly to CL-9673. Hydrolysis is the main pathway of degradation. Review of leaching data suggest that CL-9673 has the characteristics of a potential leacher. The field dissipation studies are adequate to support a conclusion on the fate of Pyridate and its degradate.

Ecological Characteristics

Technical Pyridate

Avian acute toxicity:

Bobwhite Quail	LD_{50} >1269 mg/kg

Avian dietary toxicity:

Bobwhite Quail	LC_{50} >5000 ppm
Mallard Duck	LC_{50} >5000 ppm

Freshwater fish acute toxicity:

Rainbow Trout	LC_{50} >1.2 ppm
Bluegill Sunfish	LC_{50} >2.1 ppm

Freshwater invertebrate toxicity:

Daphnia magna	EC_{50} 1.08 ppm

Estuarine toxicity:

Sheepshead minnow	EC_{50} >0.3 ppm
Mysid shrimp	LC_{50}/EC_{50} >0.3 ppm
Quahog clam	EC_{50} 0.145 ppm

Acute Contact toxicity:

Honey bee	LD_{50} >100 ug/bee

Formulation (45 WP)

Avian reproduction toxicity:

Bobwhite Quail	NOEL 1600 ppm
Mallard Duck	NOEL 640 ppm

Estuarine toxicity:

Mysid shrimp	EC_{50} 3.8 ppm

Degradate CL-9673

Freshwater invertebrate toxicity:

Daphnia magna EC_{50} 26.14 ppm

There are no outstanding data requirements based on the proposed uses on cabbage, corn and peanuts. Pyridate is slightly toxic to practically non-toxic to birds on an acute and dietary basis, moderately toxic to freshwater fish, highly toxic to estuarine fish, and moderately toxic to aquatic invertebrates.

Endangered Species

The use of Pyridate is unlikely to affect endangered terrestrial species (birds, mammals, reptiles and terrestrial stages of amphibians) because the maximum levels do not exceed the acute endangered species triggers. Exposure to aquatic organisms is estimated to be less than the endangered species trigger values for fish and aquatic invertebrates. Therefore, no endangered species review is needed for this product.

TOLERANCE ASSESSMENT

Tolerances have been established for residues of Pyridate [o-(6-chloro-3-phenyl-4-pyridazinyl)-S-octyl-carbonothioate], the metabolite 6-chloro-3-phenyl-pyridazine-4-ol and conjugates of 6-chloro-3-phenyl-pyridazine-4-ol in a variety of raw agricultural commodities (40 CFR 180.).

Cabbage	0.03 ppm
Corn; grain, forage, silage, fodder	0.03 ppm
Peanuts; nutmeat, hulls	0.03 ppm

There are no tolerances established for residues of Pyridate in/on cabbage, corn and peanuts in Canada, Mexico or by Codex.

Summary of Other Permanent Tolerances for Pyridate

No other permanent tolerances have been established for Pyridate.

Summary of Regulatory Positions

Notwithstanding EFGWB's assessment of CL-9673 as appearing to have characteristics of known groundwater contaminants, they deferred to FHB for a determination, if from a regulatory standpoint, a small scale prospective groundwater monitoring study was needed. Given that leaching of the main degradate is likely to occur in only the most extraordinary circumstances, and the fact that from a toxicological view point there should be little concern about its hazards, it is recommended that the only condition of

registration be the submission of an upgraded anaerobic metabolism study, and a small scale prospective ground-water monitoring study.

Required Unique Labeling

Precautionary Statements:

ENVIRONMENTAL HAZARDS

"This pesticide is toxic to estuarine organisms"

Use Directions:

Tough 45 WP

USE ON CABBAGE

Preharvest Interval Statement:
"Do not apply to cabbage within 45 days of harvest."

Restrictions:
"Do not feed treated cabbage to livestock within 45 days of application of Tough 45 WP."

USE ON FIELD CORN

Preharvest Interval Statement:
"Do not harvest within 68 days of application."

Restrictions:
"Do not graze or otherwise feed treated corn grain, forage, or fodder to livestock within 68 days of application of Tough 45 WP."

Tough 3.75 EC

USE ON PEANUTS

Preharvest Interval Statement:
"Do not treat within 68 days of harvest."

Restrictions:
"Do not graze or otherwise feed treated peanut hay and peanut vines to livestock."
"Do not apply when conditions favor drift which can carry spray to adjacent sensitive non-target areas."

USE ON FIELD CORN

Preharvest Interval Statement:
"Do not harvest within 68 days of application."

Restrictions:

"Do not graze or otherwise feed treated corn grain, forage, or fodder to livestock within 68 days of application of Tough 3.75 EC."

Summary of Major Data Gaps

Toxicology

NONE

Environmental Fate/Exposure

NONE

Product Chemistry (Technical)

NONE

Product Chemistry (Formulations)

NONE

CONTACT PERSON AT EPA

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